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COMPOSITION OF LEAD HALIDE POLLUTION AEROSOLS

John W. Winchester

Michigan University

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THE UNIVERSITY OF MICHIGAN

COLLEGE OF ENGINEERING

Department of Meteorology and Oceanography

Progress Report No. 1

COMPOSITION OF LEAD HALIDE POLLUTION AEROSOLS

John W. Winchester
Principal Investigator

ORA Project 01173

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SUMMARY

AP 00585-01: Composition of Lead Halide Pollution Aerosols
Principal Investigator: John W. Winchester, University of Michigan
Progress Report for the First Grant Year, Ending 31 May 1968.
Report Prepared 15 August 1968

The study of the composition of lead halide pollution aerosols has begun with an approach of environmental sampling and high sensitivity chemical analysis designed to reveal effects related to chemical reactivity of the particles in the atmosphere. Laboratory facilities have been developed for the determination of lead by anodic stripping voltammetry (ASV) and of the halogens by neutron activation analysis (NAA). Atmospheric sampling of particles has been carried out with cascade impactors by Scientific Advances, Columbus, Ohio, and Andersen Sampler, Provo, Utah, and the latter have been found to be the most satisfactory for this investigation from the standpoint of cost, ease of sampling, and ease of sectioning the samples for replicate analysis. Samples are now being taken mainly in three locations in the Great Lakes Basin: (1) Ann Arbor, Michigan, to search for the influence of Detroit 45 miles to the east as a pollution source; (2) Stations in Chicago and Gary to determine the composition of aerosols from this source region and any areal variation within it; and (3) Over waters of southern Lake Michigan from shipboard to search for the influence of Chicago and Gary to the southwest. Elements being determined in all samples are lead, copper, and cadmium by ASV and chlorine, bromine, and iodine by NAA. Preliminary results indicate distinctive particle size distributions for these elements.

DETAILED REPORT

1. Introduction.

A study of the composition of lead halide pollution aerosols is significant in several ways, some of which were recognized in 1966 when the present program was conceived and some of which have only subsequently been seen. As indicated in the original proposal to the USPHS (16), evidence has been obtained from our earlier measurements (1-10) that the lead halide aerosol formed during the combustion of ethyl fluid (13) is deficient in bromine but not in chlorine. This evidence comes from careful environmental sampling in areas where the natural halogen background is not too great (12) and by using high sensitivity methods for determining both the halogens and lead (11, 21). Although the distribution of pollution lead appears to be widespread (e.g. 14), the effect of strong local sources of atmospheric lead can be seen in certain favorable localities (15). In a review of additional literature on atmospheric lead we have pointed out (17) that the relations between the lead content of aerosols and their net pollution chlorine and bromine contents may be useful in tracing the source of atmospheric lead.

The general public health significance of lead in the atmosphere as well as the possible relation between solubility of the particulate material in lung tissue and halogen composition was already pointed out in the original proposal (16). A new significance is seen from the work of Schaeffer (18, 19) where there is a possibility that lead-containing aerosols may react with atmospheric iodine and form ice nuclei which could affect the weather. In this connection knowledge of whether iodine is an atmospheric pollutant exhibiting locally high concentrations would be important. The recently reported "La Porte weather anomaly" (20) adds further interest to the complex question of how aerosols affect the weather and whether lead in the aerosols plays a role.

In planning the research programs of the first grant year, ending 31 May 1968, prime consideration has been given to formulation

of thesis-size problems within the scope of the overall project as part of the graduate study programs of Ph.D. candidate students. Three doctoral thesis students are now working on research problems wholly or in part under this grant, and summaries of their work are given below. Because this grant was funded late, beginning in July 1967, this progress report represents work accomplished during the 1967-68 academic year.

The air and water chemistry program of the Department of Meteorology and Oceanography was initiated in January 1967 when the principal investigator (J.W.W.) joined the department. Most of the effort under the present grant during its first year has been devoted to building laboratories, to establishing analytical procedures, to attracting students in the department to join the program, and to training them in the research methods needed for this work. Dr. Wayne R. Matson, who joined the project as Research Associate in January 1968, has aided considerably in this work. At the time of this writing (15 August 1968) the results of analyses of samples collected during the spring of 1968 are ready for reporting.

2. Short time variation of the concentrations of lead and related trace metals in pollution aerosols. By using high sensitivity analytical methods of anodic stripping voltammetry and neutron activation it is possible to fractionate aerosols with a cascade impactor and gather enough sample in times of the order of an hour for analysis. This sensitivity opens up the possibility of studying hourly time variations of trace element concentrations in the aerosol size fractions. We tested this by a series of two-hour samples taken on the roof of our laboratory building in Ann Arbor and found large concentration variations which correlated with wind direction from Detroit over the 42-hour sampling period. This result forms the basis of much of our current work and planning. An abstract summarizing the major conclusions of this pilot experiment is given on the following page (24), and a complete manuscript is in preparation.

Abstract submitted for paper to be presented at the 49th Annual Meeting of the American Meteorological Society, January 20-23, 1969, New York, session on atmospheric chemistry, John W. Winchester and Julian Shedlovsky, co-chairmen.

TIME VARIATIONS OF LEAD, COPPER, AND CADMIUM AEROSOL CONCENTRATIONS IN ANN ARBOR, MICHIGAN

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The atmosphere in Ann Arbor (70 km west of Detroit) was sampled for aerosols for two-hour periods over a 42-hour interval Friday to Sunday, April 26-28, 1968, using a modified seven-stage Andersen cascade impactor and backup filter. The eight particle size fractions from each sampling were analyzed separately for lead, copper, and cadmium by means of ultra-sensitive anodic stripping voltammetry (ASV). Average particle size distributions for each of the three elements showed approximately equal masses per impactor stage (covering a factor of two radius interval) over $r \sim 0.1\text{-}10\mu$, but Pb showed a significantly greater proportion of its total concentration in particles of $r \lesssim 0.1\mu$ than did Cu or Cd. Detailed differences in size distribution from sample to sample for Cu and Cd were similar and differed from those for Pb. Substantial parallel time variations in total concentrations were seen in the ranges $2000 > Pb > 200$ ng/m^3, $200 > Cu > 7$ ng/m^3, and $130 > Cd > 7$ ng/m^3. Two prominent maxima were observed at 0200-0600 and 2000-2400 EST, April 27, correlated with a wind shift from north to east. Concentration minima at 1200-1600, April 27, and 0800-1200, April 28, correlate partially with a wind shift from east to north and west and were deeper for Cu and Cd than for Pb. The results suggest that Cu, Cd, and most of the Pb at the maximum times came from Detroit by easterly winds and that a two-hour sampling period is adequate for correlating chemical changes in the environment with mesoscale meteorological parameters.

3. Halogen and lead composition of aerosol particles over Lake Michigan. An important aspect of the atmospheric chemistry the halogens derived from pollution sources, e.g. the combustion of ethyl fluid, is the distinction between this halogen component and the halogens present naturally in the atmosphere. Moreover, the chemical exchange between these two components by atmospheric chemical reactions of particles and gases may or may not be complete in times of the order of atmospheric residence times. Our previous analyses of aerosol size fractions indicated that the particle size distribution of iodine, bromine, and chlorine were not identical and that these distributions gave a measure of chemical reactivity of these elements in the atmosphere.

As part of his Ph.D. thesis research program, Mr. Ronald H. Loucks is studying the halogen content of aerosols in the Great Lakes area by sampling with a cascade impactor and analysis by neutron activation. An especially interesting sampling location is over Lake Michigan itself from shipboard. In southerly winds the pollution component is expected to be maximum because of the direction of the heavily populated areas, but in northerly winds there is a chance that the natural component is dominant. We have tested this thinking by means of a cruise on the University of Michigan research vessel Inland Seas, and an extended abstract of these preliminary results is given on the following pages (25). This work complements a study of the composition of Great Lakes waters (23).

THE HALOGEN COMPOSITION OF AEROSOL PARTICLES OVER LAKE MICHIGAN

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Condensation of paper submitted for presentation at the 1968 International Conference Modern Trends in Activation Analysis, October 7-11, 1968, National Bureau of Standards, Gaithersburg, Maryland.

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INTRODUCTION

The halogen elements chlorine, bromine, and iodine are distributed in the atmosphere between particulate and gaseous phases and show evidence of chemical reactivity which affects the variation of chemical composition with particle radius in the stable aerosol range of 0.2 to 20 microns. Previously published analyses of naturally-occurring aerosols for halogens are restricted almost entirely to samples collected in coastal locations of the U.S. where local sources of sea salt are present [1, 2, 3, 4]. In this investigation we are undertaking the first extensive sampling in the inland U.S. in regions where both natural and pollution sources of the halogens may be important. The results are to be compared with earlier studies of both naturally-occurring aerosols and aerosols containing lead of pollution origin [5, 6, 7].

High sensitivity means of chemical analysis are employed in order to permit sampling of cubic meter volumes of air which can be fractionated into particles of different sizes and permit sampling times of a few hours or less. The halogens are determined by neutron activation [8] and lead and certain other trace metals are determined using anodic stripping voltammetry [9, 10]. Particle size sorting is accomplished using cascade impactors of six or more stages with polyethylene impaction surfaces suitable for activation analysis and for trace metal removal using ultrasonic vibration.

EXPERIMENTAL

As the principal objective of the sampling program, a field location was selected which would not have local sources of halogens, lead, and other trace metals of interest but with well-defined pollution sources at some distance removed as well as a regional natural distribution of these elements in the atmosphere. Sampling above the surface of Lake Michigan from the deck of the research vessel Inland Seas operated by the University of Michigan was viewed as affording

detection of air pollutants emanating from coastal locations, in particular the Chicago-Gary urban and industrial complex when winds were from the south, or the determination of the natural background of these elements, especially when the winds were from the north. During May 1968 a cruise was carried out where samples of aerosol particles were collected during two daylight traverses between Grand Haven, Michigan, and Chicago, Illinois, and during a continuous 24-hour sampling period overnight in the middle of the southern basin of Lake Michigan. During this time the winds varied from northerly to southerly.

Aerosol sampling was carried out using a Scientific Advances six-stage cascade impactor and an Andersen sampler, both devices resolving particles into groups differing by about a factor of two in radius in the stable aerosol range. Impaction on the surfaces of polyethylene inserts was judged to be efficient in the moist atmosphere over the lake. Possible contamination from the ship smoke-stack was monitored by Hi-Vol filter samplers operating in various places on the ship, and by the degree of darkening of some of the filters the impactor locations were selected so as to be free of contamination.

Chemical analysis for halogens was carried out by neutron activation of the polyethylene inserts, washing, and separation of I, Br, and Cl using solvent extraction followed by beta counting. Analysis for Pb, Cd, and Cu was performed by anodic stripping voltammetry using a composite mercury graphite electrode. Polyethylene inserts used in the Andersen sampler were cut into two portions, one for neutron activation and one for anodic stripping, the latter processed by desorbing the trace metal deposit into high purity aqueous NaCl solution using ultrasonic vibration. The sensitivity of both methods of analysis is adequate to determine these elements in all but the cleanest air using a few cubic meters of air volume passed through the impactor stages in several hours or less.

The locations and circumstances of the individual runs are given in Figure 1 and Table 1. Runs 8 and 9 were taken while the ship was lying motionless without power in the middle of the southern basin of

Lake Michigan and runs 3 and 4 while the ship was at rest in a harbor of south Chicago, an urban and industrial location a few kilometers from the lake shore. The other samples were taken while the ship was underway over the stretches of water and during the times indicated.

RESULTS AND DISCUSSION

A summary of the halogen results is given in Tables 2, 3, and 4. In all cases the six Scientific Advances cascade impactor stages and the backup filter were analyzed individually for seven separate data points per sampling run. Because of lack of space only a summary of these data is presented in the tables. The data for lead are not yet available at this writing.

Two major observations should be made in scanning the data for iodine in Table 2. (1) A large fraction of the iodine is held by particles of radius less than 0.25 micron without apparent systematic differences due to location, winds, or relative humidity. (2) The total iodine concentration does not vary with proximity to the Chicago-Gary urban-industrial area or with winds which could carry pollutants from that area to the sampling location, and the total iodine concentrations observed compare favorably with those observed in Hawaii and in polluted as well as unpolluted locations in Fairbanks, Alaska. Therefore, we do not observe iodine to have significant air pollution sources associated with urbanization.

The data for bromine in Table 3 indicate (1) that a large fraction of bromine is contained on particles of radius less than 0.25 micron, and there is no apparent systematic variation of this tendency with location, winds, or relative humidity. However, (2) the bromine values in Calumet Harbor are very much greater than the samples collected over the lake, strongly suggesting an urban pollution origin of much atmospheric bromine. The Fairbanks pollution average is not far from these values. The lake runs showed similar values independent of wind direction, but it should be borne in mind that the wind speeds

were very mild during this sampling cruise. The similarity of these values with Fairbanks and Hawaii background values suggests that this bromine concentration is predominantly natural.

The chlorine data, Table 4, (1) show negligible amounts held by particles smaller than 0.25 micron radius for the samples collected over the lake, and in the majority of cases at least a third of the chlorine is held by particles above 1 micron in radius without apparent correlation with the meteorological parameters of Table 1. (2) The two Calumet Harbor samples contrast by showing not only greatly higher concentrations than any of the other runs but a substantial fraction of chlorine in the smallest particle size fraction. A local pollution source is suggested, and, because the concentration is so much greater than observed in the Fairbanks pollution study, we ascribe this tentatively to an industrial source other than automotive or other fuel combustion. (3) The average of lake samples is similar to the Fairbanks area background values, and these concentrations may represent natural chlorine aerosol levels.

In general, by comparison with the Hawaii and Fairbanks data, the Lake Michigan data suggest that natural concentration levels have been detected in many of the samples. The presumably natural bromine and iodine are carried to a great extent by the smallest size particles, in contrast to chlorine which is on mainly larger size particles. There is no evidence that iodine is a significant air pollutant associated with the urban or industrial areas tested, but both bromine and chlorine show anomalously high concentrations in the urban localities. The atmospheric input of bromine may be largely the result of burning leaded gasoline, but the inputs of chlorine may be from various urban and industrial sources. The question of atmospheric residence times and removal rates must await further sampling and analysis before answering.

ACKNOWLEDGEMENTS

This work was supported in part by contract AT(11-1)-1705 with the U.S.A.E.C., grant AP-00585 from the U.S.P.H.S., facilities grant GA-811 from the N.S.F., and a grant from the Phoenix Memorial Fund of the University of Michigan. We are grateful for the use of the University of Michigan ship Inland Seas, and one of us (R.H.L.) is indebted to the Bedford Institute of Oceanography, Nova Scotia, for partial salary support to carry out this work.

REFERENCES

[1] Duce, R. A., Winchester, J. W., and Van Nahl, T. W., J. Geophys. Res. 70, 1775 (1965).

[2] Duce, R. A., Winchester, J. W., and Van Nahl, T. W., Tellus 18, 238 (1966).

[3] Winchester, J. W., and Duce, R. A., Tellus 18, 287 (1966).

[4] Duce, R. A., Woodcock, A. H., and Moyers, J. L., Tellus 19, 369 (1967).

[5] Lininger, R. L., Duce, R. A., Winchester, J. W., and Matson, W. R., J. Geophys. Res. 71, 2457 (1966).

[6] Winchester, J. W., Zoller, W. H., Duce, R. A., and Benson, C. S., Atmospheric Environment 1, 105 (1967).

[7] Winchester, J. W., and Duce, R. A., in Nuclear activation Techniques in the Life Sciences, I.A.E.A., Vienna, 1967, pp. 631-43.

[8] Duce, R. A., and Winchester, J. W., Radiochim. Acta 4, 100 (1965).

[9] Matson, W. R., Roe, D. K., and Carritt, D. E., Anal. Chem. 37, 1594 (1965).

[10] Matson, W. R., and Roe, D. K., in Analysis Instrumentation, Vol. 4, Plenum Publishing Corp., 1967.

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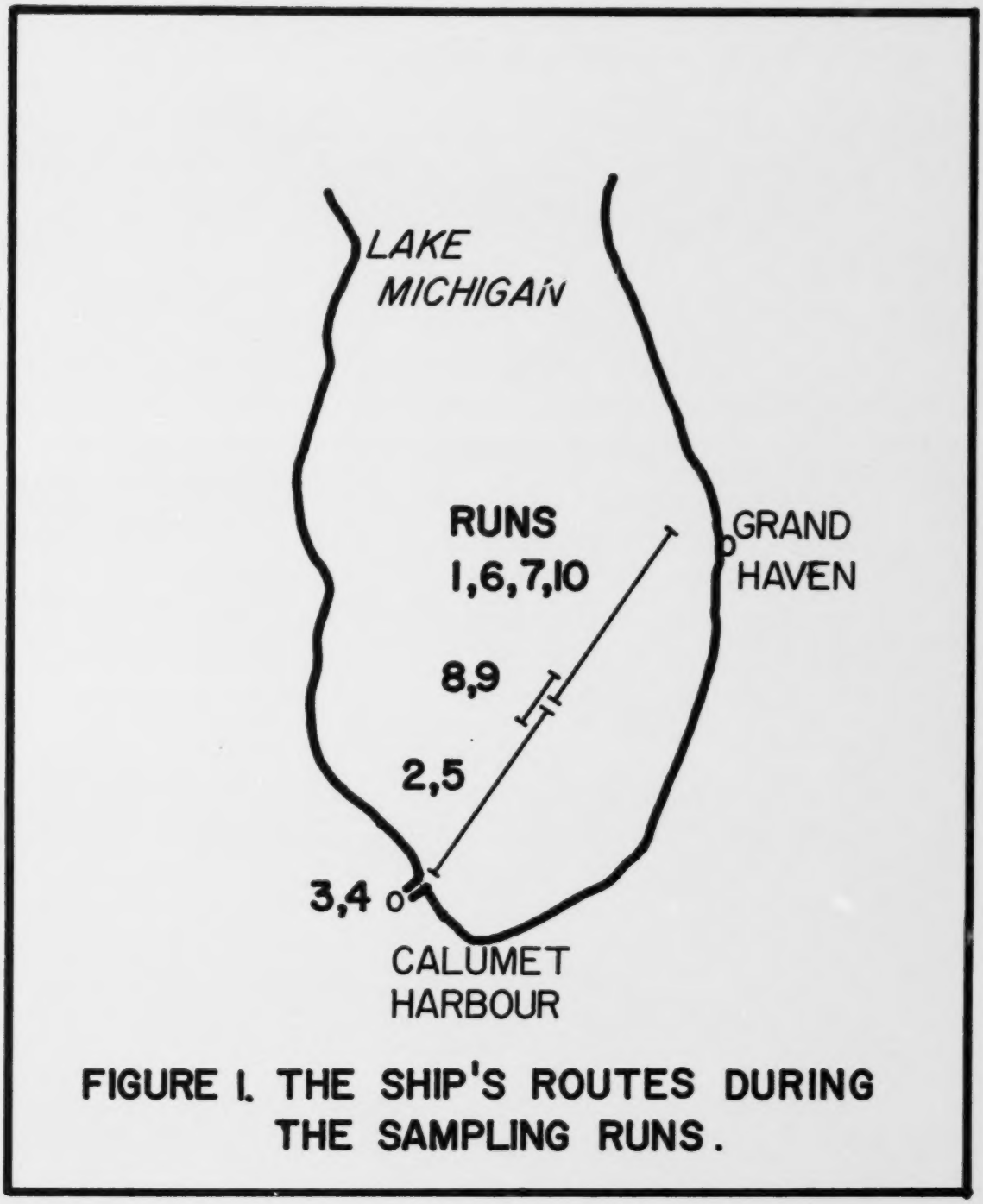

FIGURE I. THE SHIP'S ROUTES DURING THE SAMPLING RUNS.

Table 1

Circumstances of the Runs

Run[a]	Date, 1968	Time, EST	Wind, m/s	R.H., %	Clouds
1	May 20	0722-1156	NW @ 5	85	4/8
2	May 20	1225-1606	NW @ 5	80	4/8
3	May 20-21	1652-0224	NNW @ 5	75	0
4	May 21	0307-0559	W @ 5	95	0
5	May 21	0640-1102	SW @ 3	85	1/8
6	May 21	1124-1450	SW @ 3	85	1/8
7	May 22	0633-1033	SSE @ 3	98	7/8
8	May 22	1102-1912	SSE @ 2	80	fog
9	May 22-23	1940-0614	Var. @ 3	98	8/8, rain
10	May 23	0650-0952	ENE @ 4	100	8/8

[a]For locations see Figure 1 and text.

Table 2

Iodine Concentrations

Run	Total concentration ng/m^3	Per cent of total with radius $<0.25\mu$
1	7.4 ± 0.7	70
2	1.0 ± 0.4	65
3	7.3 ± 0.4	52
4	1.9 ± 0.5	37
5	<0.7	>90
6	5.0 ± 0.6	64
7	1.0 ± 0.4	>90
8	1.9 ± 0.4	32
9	0.9 ± 0.2	44
10	0.7 ± 0.3	>90

Mean:	3 ± 1
Fairbanks background:	3.0 ± 0.3[a]
Fairbanks pollution:	3.9 ± 0.3[a]
Hawaii background:	$\geq$1.7[b]

[a]Means of 10 rural samples and 20 city samples collected by Millipore filter in and around Fairbanks, Alaska, during winter [6, 7].

[b]Mean of 8 samples collected at the seashore by cascade impactor but without backup filter [4].

Table 3

Bromine Concentrations

Run	Total concentration ng/m^3	Per cent of total with radius <0.25μ	Per cent of total with radius <0.5μ
1	24 ± 3	91	94
2	11 ± 1	50	75
3	1380 ± 90	61	77
4	407 ± 20	29	64
5	22 ± 2	50	89
6	13 ± 2	80	80
7	27 ± 2	56	78
8	42 ± 2	45	68
9	31 ± 2	46	79
10	22 ± 1	51	74

Mean of runs 3 and 4:	~900
Mean of the other runs:	24 ± 4
Fairbanks background:	35 ± 3[a]
Fairbanks pollution:	500 ± 50[a]
Hawaii background:	≥11[a]

[a]See notes to Table 2.

Table 4

Chlorine Concentrations

Run	Total concentration $\mu g/m^3$	Per cent of total with radius <0.25μ	<0.5μ	<1μ
1	0.26 ± 0.04	<4	6	21
2	0.15 ± 0.02	<6	39	69
3	9.6 ± 1.0	58	83	89
4	12.2 ± 1.6	28	74	85
5	0.21 ± 0.03	<5	64	74
6	0.28 ± 0.03	<4	23	51
7	0.71 ± 0.04	<2	20	48
8	1.11 ± 0.06	<1	10	35
9	0.26 ± 0.02	<4	49	49
10	0.70 ± 0.05	<2	13	68

Mean of runs 3 and 4:	~11
Mean of the other runs:	0.5 ± 0.1
Fairbanks background:	0.5 ± 0.03[a]
Fairbanks pollution:	1.4 ± 0.2[a]
Hawaii background:	$\geq$3.6[a]

[a]See notes to Table 2.

4. Areal distribution of pollution trace metal concentrations in the Chicago-Gary urban complex. In the literature on atmospheric lead and other trace metal pollutants contained in aerosols we have found little attention paid to the geographic distribution of concentrations over a metropolitan area, but we feel that a study of the migration outward of these substances must be based on a good understanding of the sources within the urban region. The southern Lake Michigan vicinity is an ideal locality for this study because of the possibility of sampling outward from the cities over the lake where local sources are minimal and a true idea of the dispersion processes may be obtained. Furthermore, recent documentation of the anomalously high rainfall east of Gary, known as the La Porte weather anomaly (20) and ascribed to interaction of pollutants with lake water vapor, makes a study of pollution aerosol composition timely.

With this in mind, Mr. Paul Harrison has chosen as his Ph.D. thesis topic the documentation of aerosol concentrations of lead, copper, cadmium, bismuth, and additional trace metals in the Chicago-Gary source area. Analysis of filter samples is being carried out using anodic stripping voltammetry for the elements mentioned and using atomic absorption spectrophotometry for the additional metals. Portions of filter samples from about 50 stations have been or will be obtained for analysis from the air pollution control districts of Chicago, Gary, and Hammond and from Valparaiso University and the Argonne National Laboratory. Five different days from June to August 1968 have been chosen as times when 24-hour samples were taken simultaneously at all of the stations and can be made available to us. On some of these days we collected additional aerosol samples from our University of Michigan research vessel over southern Lake Michigan. On all of these days meteorological information is available to aid in interpreting any differences in distributions found.

As a pilot study for this sampling program, a series of about 35 samples were obtained from air filter sampling stations in Chicago and Gary operating on May 20 or 21, 1968, during predominantly northwesterly winds. These have been analyzed for lead, copper,

cadmium, and bismuth, and the results have been plotted on maps of the vicinity. Although it is premature for a formal report of these results, certain regularities stand out in the patterns of concentration distribution. (1) Strong signals above analytical blanks are observed in many of the samples, but others are very low and nearly at values determined by the composition of the filter material, so that there is a distinct non-uniformity of concentration of all four elements in the metropolitan region. (2) The high and low values fall into patterns which can be contoured with little complication due to anomalous single values. (3) The contours of lead show a more or less smoothly varying concentration in Chicago which decreases gradually toward northeastern Indiana. The levels found in the northwest part of Chicago are considerably lower than expected on the basis of population distribution and apparently reflect migration of aerosols in the northwest winds toward the southeast. A broad maximum in lead concentration is observed in south central Chicago. (4) Copper and cadmium both show strong maxima in Gary having closely spaced oval contours around their centers with major axis normal to the lake shore. Concentrations throughout Chicago are generally very much less than in Gary, in contrast to lead which is more abundant in Chicago than in Gary. (5) The centers of maximum concentration of copper and cadmium are not exactly the same suggesting that the principal sources, though both located in the Gary area, are actually different. The copper-bearing particles may migrate at different rates in the atmosphere than particles bearing cadmium; both meteorological and industrial factors may be involved.

5. An experimental and theoretical study of the size distribution and residence time of lead in the atmosphere. Of importance in the interpretation of the concentrations of lead observed in the atmosphere is an understanding of the processes for its removal and its residence time under different atmospheric conditions. Particle size distribution of lead in aerosols is a parameter which may aid in this understanding since removal processes may be particle size dependent

and particle size may increase by coagulation if time is sufficient. Lead aerosols are formed by fuel combustion largely with radii of 0.2 microns or less according to our observations and to the published work (reviewed in reference 22) and are therefore smaller than particles which contain most of the sea salt, rock dust, and other common materials in the atmosphere. Consequently we cannot assume that the efficiency of cleansing of the atmosphere with respect to lead is the same as for other materials of different particle size distribution or is the same for lead aerosols of any age.

Mr. Dale Gillette has chosen for his Ph.D. thesis research problem an examination of these questions. The experimental part of his work includes aerosol collection using a seven-stage Andersen sampler with back-up filter and chemical analysis by anodic stripping voltammetry. He is attempting to explore the widest variety of atmospheric conditions possible during the time available, such as urban air, air over Lake Michigan, air in remote regions, air before and after rain and during fog, and sampling during the day and night. By this work he expects to document the range of variation of lead aerosol size distributions and gain insight into the important meteorological factors affecting them. Then the second part of the project will be to apply theoretical knowledge of coagulation and removal processes to a rate study of the parameters describing atmospheric lead. Mr. Gillette, whose research began a few weeks before the closing date for this report, has already analyzed test samples which demonstrate that measurable variations occur in the size distribution of atmospheric lead aerosols.

6. Facilities developed for this program. The major effort for the first grant year has been to develop a new chemical program in the Department of Meteorology and Oceanography where there previously had been none. Apparatus for anodic stripping voltammetry (ASV) for lead determination and a gas chromatograph have been purchased from funds provided by this grant from the USPHS. Laboratory apparatus for radiation measurement in neutron activation analysis (NAA) and an

atomic absorption spectrophotometer have been provided by NSF Grant GA-811. A cascade impactor and some additional air sampling equipment have been purchased both from this grant and under a contact with the USAEC, AT(11-1)-1705, for use by both programs. We now have a well-equipped laboratory for the work of this investigation.

During this time several graduate students have been attracted into the air and water chemistry program in the Department of Meteorology and Oceanography, some of whom are involved in the work of the present USPHS grant. Though these students are not primarily chemists, they have learned to carry out chemical analyses of samples according to our established procedures and to apply these techniques to their specialties. The role of a post-doctoral Research Associate analytical chemist as part of the group is critically important for ultimate success, and Dr. Wayne R. Matson, who joined our department in January 1968, has been instrumental in providing the tutorial instruction in analytical chemical techniques to these students.

7. Persons active on this project during the first grant year ending 31 May 1968.

Wayne R. Matson, Ph.D., Research Associate, supported half-time on this project and half-time by contract AT(11-1)-1705 with the USAEC, 4 1/2 months effort (January-May 1968).

Paul R. Harrison, Ph.D. candidate, supported in part as an Air Pollution Trainee through a grant from the NIH. Full-time effort on this project 4 months (February-May 1968).

Dale A. Gillette, Ph.D. candidate, supported in part as an Air Pollution Trainee through a grant from the NIH. Full-time effort on this project 2 months (April-May 1968).

Ronald H. Loucks, Ph.D. candidate, supported in part by the Bedford Institute of Oceanography, Dartmouth, Nova Scotia, from which he is on leave, and in part by the USAEC. Half-time effort on this project 10 months (August 1967-May 1968).

8. Bibliography. References 24 and 25 below are reports of work supported in part by this grant, AP-00585-01.

1. Duce, R. A., J. T. Wasson, J. W. Winchester, and F. Burns, Atmospheric iodine, bromine, and chlorine, J. Geophys. Res., 68, 3943-3947, 1963.
2. Duce, R. A., J. W. Winchester, and T. W. Van Nahl, Iodine, bromine, and chlorine in the Hawaiian marine atmosphere, ibid., 70, 1775-1799, 1965.
3. Lininger, R. L., R. A. Duce, J. W. Winchester, and W. R. Matson, Chlorine, bromine, iodine, and lead in aerosols from Cambridge, Massachusetts, ibid., 71, 2457-2463, 1966.
4. Duce, R. A., J. W. Winchester, and T. W. Van Nahl, Iodine, bromine, and chlorine in winter aerosols and snow from Barrow, Alaska, Tellus, 18, 238-248, 1966.
5. Winchester, J. W., and R. A. Duce, Coherence of iodine and bromine in the atmosphere of Hawaii, northern Alaska, and Massachusetts, ibid., 18, 287-292, 1966.
6. Winchester, J. W., W. H. Zoller, R. A. Duce, and C. S. Benson, Lead and halogens in pollution aerosols and snow from Fairbanks, Alaska, Atmospheric Environment, 1, 105-119, 1967.
7. Winchester, J. W., and R. A. Duce, The global distribution of iodine, bromine, and chlorine in marine aerosols, Die Naturwissenschaften, 5, 110-113, 1967.
8. Winchester, J. W., and R. A. Duce, Halogen geochemistry, Tech. Eng. News, 47, No. 3, 27-31, 1965.
9. Winchester, J. W., and R. A. Duce, Geochemistry of iodine, bromine, and chlorine in the air-sea-sediment system, Symposium on Marine Geochemistry Proceedings, University of Rhode Island, 1965.
10. Duce, R. A., and J. W. Winchester, Determination of iodine, bromine, and chlorine in atmospheric samples by neutron activation analysis, Radiochim. Acta., 4, 100-104, 1965.
11. Matson, W. R., D. K. Roe, and D. E. Carritt, Composite mercury-graphite electrode for anodic stripping, Anal. Chem., 37, 1594, 1965.
12. Junge, C., Air Chemistry and Radioactivity, Academic Press, New York, 1963.

13. Rose, A. H., Jr., Automotive exhaust emissions, in Air Pollution, Vol. 2, edited by A. C. Stern, Academic Press, New York, 1962.
14. Patterson, C. C., Contaminated and Natural Lead Environments of Man, Archives of Environmental Health, 11, 344, 1965.
15. Benson, Carl S., Ice fog: low temperature air pollution, UAG R-173, Geophysical Institute, University of Alaska, College, Alaska, November 1965.
16. Winchester, J. W., "Composition of Lead Halide Pollution Aerosols," proposal to U.S. Public Health Service for research grant AP-00585-01, 13 July 1966.
17. Winchester, J. W., and R. A. Duce, "Neutron activation analysis of lead halide pollution aerosols," Nuclear Activation Techniques in the Life Sciences, pp. 631-643, I.A.E.A., Vienna, 1967.
18. Schaeffer, V. J., Ice nuclei from automobile exhaust and iodine vapor, Science, 154, 1555, 1966.
19. Schaeffer, V. J., The detection and measurement of submicroscopic particles of lead oxide and of iodine molecules in the free atmosphere, Bull. Am. Meteorol. Soc., 48, 27, 1967.
20. Changnon, Stanley A., The La Porte weather anomaly--fact or fiction?, Bull. Am. Meteorol. Soc., 49, 4, 1968.
21. Matson, W. R., and D. K. Roe, in Analysis Instrumentation, Vol. 4, Plenum Publishing Company, 1967.
22. Winchester, J. W., Lead pollution, in 1969 Yearbook of Science and Technology, McGraw-Hill (in press).
23. Tiffany, M. A., J. W. Winchester, and R. H. Loucks, Natural pollution sources of iodine, bromine, and chlorine in the Great Lakes, Water Pollution Control Federation, September 1968 Annual Conference (Abstract in press).
24. Harrison, P. H., W. R. Matson, and J. W. Winchester, Time variations of lead, copper, and cadmium aerosol concentrations in Ann Arbor, Michigan, Bull. Am. Meteorol. Soc., (Abstract in press).
25. Loucks, R. H., J. W. Winchester, W. R. Matson, and M. A. Tiffany, The halogen composition of aerosol particles over Lake Michigan, Modern Trends in Activation Analysis, I.A.E.A. Symposium Proceedings, (in press).